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MORIWAKI YUTAKA**(54) PRODUCTION OF SINTERED APATITE CARBONATE****(55)Abstract:**

PURPOSE: To easily and economically obtain a sintered apatite carbonate having a carbonate group content comparable to the content in a hard bio-tissue and having high mechanical strength sufficient for the use as a filling material for organism such as bone, dental, filling and prosthetic material.

CONSTITUTION: Apatite carbonate powder having a carbonate group content of 5-30wt.%, an average particle diameter of $\leq 5 \mu\text{m}$ and a BET value of 10-50m²/g is sintered at 600-850° C.

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CLAIMS

[Claim(s)]

[Claim 1]A manufacturing method of an apatite carbonate sintered compact characterized by making it sinter at temperature of 600 ** - 850 ** using apatite carbonate powder whose carbonic acid group content is 5 to 30 % of the weight, and whose BET value mean particle diameter is 5 micrometers or less, and is $10\text{--}50\text{m}^2/\text{g}$.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the method of manufacturing advantageously the apatite carbonate sintered compact of the substantia compacta excellent in biocompatibility which makes it come to contain the carbonic acid group which is applied to the manufacturing method of an apatite carbonate sintered compact, especially is [abbreviated] equal to the carbonic acid group content in the living body hard tissue.

[0002]

[Background of the Invention] From the former, as apatite carbonate and hydroxyapatite which contains a carbonic acid group if it puts in another way, A type which makes it come to replace some hydroxyl groups (OH^-) of hydroxyapatite [$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$] with a carbonic acid group (CO_3^{2-}), It is known that there is a B type which replaces similarly a part of the phosphate group (PO_4^{3-}) with a carbonic acid group. And the A type apatite carbonate of them is compounded by calcinating hydroxyapatite (HAp) at the temperature of 1000 ** in atmosphere (carbon dioxide + steam), and, on the other hand, B type apatite carbonate is compounded by wet process using the salts concerned in some numbers.

[0003] By the way, it is known that the mineral constituent of the hard tissue of a vertebrate is what comprises the apatite carbonate containing about 2% – 10% of carbonic acid group in ash. And A type is intermingled about 10 to 20% in B type which dental enamel mainly described above. It is said that dental dentine and bone are close to the above-mentioned B type.

As said that dental dentine and bone are close to the above mentioned B type. Since A type apatite carbonate is compounded by hot solid phase reaction, it is stable also at a remarkable elevated temperature, but. Since it is difficult for B type apatite carbonate for a carbonic acid group to decompose and **** at an elevated temperature, and also to make it sinter at low temperature, in order to obtain the sintered compact, Adoption of special techniques, such as calcination in the carbon dioxide atmosphere under HIP (Hot Isostatic Press), a hotpress and ultra-high pressure CIP (Cold Isostatic Press) processing, or an elevated temperature, is needed

and a high pressure (10 GPa, 1000 °C) processing, or an elevated temperature, is needed. [0004] However, if it is in the technique from the former for obtaining the sintered compact of these apatite carbonate, all, a complicated process is adopted, and apparatus cost is high and inherent in a fault, like mass production is also difficult and there is. And although it is supposed compared with HA or TCP (tricalcium phosphate) for such a fault that the direction of the apatite carbonate near the living body hard tissue is excelled more in biocompatibility, apatite carbonate is hardly used from the former as a biomechanical material.

〔0005〕

[Problem(s) to be Solved] The place which this invention makes this situation a background, succeeds in it in here, and is made into the technical problem. It is in providing the technique of the ability to manufacture easily and advantageously the apatite carbonate sintered compact excellent in biocompatibility which contains a carbonic acid group comparable as the living body hard tissue, and has sufficient mechanical strength to use it as a living body packing material like a living body's bone or dental filling material, or supplementation material.

〔0006〕

[Means for Solution] And if it is in this invention for such business solution, Using apatite carbonate powder whose carbonic acid group content is 5 to 30 % of the weight and whose BET value mean particle diameter is 5 micrometers or less, and is $10\text{--}50\text{m}^2/\text{g}$, at temperature of 600 ** - 850 **, make it make it sinter and by this. After calcination will have little desorption of a carbonic acid group, and can manufacture a precise sintered compact at low temperature comparatively.

[0007]

[Elements of the Invention] Thus, particle diameter, specific surface area (BET value), and carbonic acid group content of apatite carbonate powder are controlled by this invention in a specific range. Therefore, although the low-temperature-sintering nature is improved, with a substantially-compact apatite carbonate (600 ** - 850 **) sintered compact for medical application or dentistry which were comparatively excellent in biocompatibility by sintering operation under low temperature can be given advantageously. Apatite carbonate powder which has such the characteristic may be easily manufactured by various kinds of synthetic techniques in which a dry method, wet process, etc. are publicly known, and the synthetic method in particular is not limited.

But using apatite carbonate powder excellent in low-temperature-sintering nature manufactured using wet process, if it is in this invention is recommended, and especially starting materials in such wet process are not limited, but if they are the salts concerned, they can use all.

[0008]As wet process recommended as a synthetic method for obtaining advantageously apatite carbonate powder made into the purpose in this invention, Typically (1) calcium-nitrate 4 hydrate, dibasic sodium phosphate, And sodium bicarbonate or sodium carbonate, (2) calcium acetate, Dibasic sodium phosphate and sodium bicarbonate, or sodium carbonate, (3) Calcium hydrogen phosphate, calcium carbonate, and calcium hydroxide, (4) Calcium nitrate 4 hydrate, hydrogen phosphate ammonium and ammonium acid carbonate, or ammonium carbonate, (5) There is a method to which calcium acetate, hydrogen phosphate ammonium and ammonium acid carbonate or ammonium carbonate, (6) calcium carbonate, calcium-hydrogen-phosphate dihydrate or hydrogen phosphate dicalcium, etc. is made to react.

[0009]Anyway, as a starting material for obtaining apatite carbonate powder according to this invention, Sodium salt, ammonium salt, calcium salt, or phosphoric acid is used as a phosphoric acid raw material, As a carbonic acid raw material, calcium salt, sodium salt, ammonium salt, or carbon dioxide is used, and also as a calcium raw material, Apatite carbonate powder which a nitrate, acetate, carbonate, hydroxide, or an phosphate is used, and also hydroxyapatite powder etc. are used suitably and makes them the purpose in accordance with a synthetic technique from the former combining these combination ingredient suitably is manufactured.

[0010] And in this invention, what has preferably 5 to 30 % of the weight of carbonic acid group content in 6 to 20% of the weight of within the limits will be used as this apatite carbonate powder. If carbonic acid group content in apatite carbonate powder becomes less than 5 % of the weight, in a calcination temperature field adopted by this invention. If it is when the eburnation becomes difficult and carbonic acid group content exceeds 30 % of the weight, it is not only difficult to obtain apatite carbonate powder of such carbonic acid group content, but it cannot be said to be a

desirable thing, considering biocompatibility, a BET value as which, as for apatite carbonate powder, the mean particle diameter expresses 5 micrometers or less of 1.0 micrometers or less and specific surface areas preferably in order to close, if possible [low temperature sintering] -- $10\text{--}50\text{m}^2/\text{g}$ -- it is necessary to be $20\text{--}40\text{m}^2/\text{g}$ preferably If mean particle diameter of apatite carbonate powder becomes larger than 5 micrometers or a BET value becomes smaller than $10\text{--}m^2/\text{g}$, When it becomes difficult to obtain a precise sintered compact and a BET value becomes larger than $50\text{--}m^2/\text{g}$, since contraction is large, problems, like a crack enters easily will be caused bad [the operativity of shaping].

[0011]By the way, if apatite carbonate powder which has such the characteristic is directly obtained by suitable synthetic techniques, such as a wet synthetic method, can obtain an apatite carbonate sintered compact made into the purpose by fabricating and calcinating in predetermined shape, using it as it is, but. When a BET value of compounded apatite carbonate powder is too high, After making the BET value into a thing of this invention within the limits by carrying out temporary quenching beforehand at a suitable temperature, If it may fabricate and calcinate, and particle diameter of apatite carbonate powder is too large conversely, or it is when a BET value is too small, suitable grinding operation is performed, and it accomplishes with a thing of this invention within the limits, and shaping and calcinating are also possible using it.

[0012]And it faces manufacturing an apatite carbonate sintered compact made into the purpose using apatite carbonate powder according to this this invention, First, after molding operation is performed like a manufacturing method of the conventional sintered compact and being considered as a Plastic solid of specified shape to such apatite carbonate powder, calcination operation is performed to the acquired Plastic solid. This Plastic solid will be produced by, for example, carrying out pressing in accordance with a conventional method, after preforming apatite carbonate powder, for example, in CIP shaping, CIP pressure of 1-3 t will be adopted. According to this invention, 600 ** - 850 **, preferably, sintering temperature shall be 650-800 **, and by this. Relative density is obtained for carbonic acid group ullage, and 80 or more MPa and a high intensity substantia- compacta sintered compact of Vickers hardness 4.0GPa are obtained for three point bending intensity not less than 80% not less than 80% of former powder.

[0013]An apatite carbonate sintered compact obtained in this way contains a carbonic acid group which is [abbreviated=] equal to carbonic acid group content in living body hard tissue, and. Although it is useful as medical application which has sufficient mechanical strength to be required as supplementation material for a bone or teeth, or a filler, and was excellent in biocompatibility, or a dental material, It may be used for the target use as it is, and also such an apatite carbonate sintered compact may be used as granulation or a porous body according to a request.

[0014]

[Example]It is a place needless to say that this invention is not what also receives any restrictions by the statement of such an example although the typical example of this invention is shown below and this invention is clarified still more concretely. It should be understood that it is what can add change, correction, improvement, etc. which become various to this invention based on a person's skilled in the art knowledge unless it deviates from the meaning of this invention besides the following examples besides the further above-mentioned concrete description.

[0015]First, various kinds of apatite carbonate powder was manufactured with the wet synthetic method. That is, you made it 5L of the solution 5L (liter) in which 0.6-mol dibasic-sodium-phosphate solution is made to come to dissolve sodium bicarbonate of the specified quantity, and 1-mol calcium acetate solution simultaneously dropped at the dropping speed of 500 mL/Hr into the ion exchange water 3L held at the temperature of 80 **. In the meantime, pH of this ion

exchange water was controlled by NaOH within the limits of 9.0–9.5. And after the end of this dropping, it washed after riping for 12 hours and filtering subsequently at the temperature of 80 ** until Na ion was no longer detected. And at the temperature of 110 **, dry for 24 hours and the powder obtained by this and in a resin pot, Various kinds of apatite carbonate powder A–D which has the carbonic acid group content, the mean particle diameter, and the BET value which are shown in the following table 1 was obtained by carrying out wet milling for 24 hours, and also drying and drying using the zirconia ball of 5 mmphi. The powder E cracks the powder A with a mortar after 110 ** and 24-hour desiccation, without performing pot mill grinding, and is only powder which let an 80-mesh sieve pass.

[0016]

[Table 1]

表 1

	炭酸基含有量 (重量%)	平均粒径 μm	BET 値 (m ² /g)
粉末A	10.90	0.44	24.0
粉末B	6.60	0.42	21.8
粉末C	4.35	0.64	20.3
粉末D	1.30	0.52	36.2
粉末E	10.90	10.44	8.0

[0017]Subsequently, CIP pressure after filling up a molding die, respectively and preforming using these apatite–carbonate powder of various kinds of: CIP shaping was carried out at 3 t, and calcination operation was performed with predetermined calcination temperature into the atmosphere to the acquired Plastic solid, respectively. As a calcination program, 500 ** carries out temperature up at 2 ** a rate for /, After holding for 5 hours, temperature up is successively carried out to a predetermined temperature up to 600 ** – 900 ** at 1 ** a rate for /, And after holding at the target temperature for 5 hours, the temperature was made to lower at 1 ** a rate for / to 500 **, and was successively lowered at 2 ** a rate for / to 300 **, and also it cooled radiationally in the furnace to the room temperature, and the procedure of obtaining a sintered compact was adopted. The relative density of various kinds of sintered compacts obtained in this way is shown in the following table 2. Here, theoretical density:3.16g[/cm]³ of hydroxyapatite was made into 100% of relative density.

[0018]

[Table 2]

表 2

焼結温度 (℃)	相対密度				
	粉末A	粉末B	粉末C	粉末D	粉末E
600	80.4	70.6	61.4	55.0	焼結せず
650	91.1	83.2	69.0	55.1	焼結せず
700	95.9	90.2	69.0	55.1	焼結せず
750	95.2	94.6	69.6	55.4	焼結せず
800	92.7	94.6	69.6	56.6	焼結せず
850	88.6	94.3	69.9	57.3	焼結せず
900	60.4	90.2	焼結せず	59.8	焼結せず

[0019]The characteristic of residual carbonic acid of the sintered compact obtained using the apatite carbonate powder A, i.e., the amount, three point bending intensity, a fracture toughness value, Vickers hardness, and bulk density are evaluated, and the result is shown in the following table 3.

[0020]

[Table 3]

表 3

焼成 温度 (℃)	残存 炭酸量 (WT%)	3点曲 げ強度 (MPa)	破壊粉性値 (K_{Ic} , $MPa^{1/2}$)	ヴィッカ ース硬さ (GPa)	かさ密度 (g/cm ³)	相対 密度 (%)
600	89.4	32	0.51	1.6	2.54	80.4
650	86.2	82	0.72	4.0	2.88	91.1
700	85.8	94	0.70	4.9	3.03	95.9
750	84.4	98	0.80	4.7	3.01	95.2
800	82.6	91	1.03	4.0	2.93	92.7
850	82.2	58	1.44	2.6	2.80	88.6
900	73.8	29	測定不能	0.4	1.91	60.4

[0021]If it is in the thing using the apatite carbonate powder A and B according to this invention so that more clearly than the above result, To an effective precise object being acquired within the limits of 600 ** - 850 **, in the apatite carbonate powder C, D, and E which has the characteristic besides the range of this invention, it does not elaborate or does not sinter at all in such a temperature range. That is, when carbonic acid group content is little powder like the apatite carbonate powder C and D, even if mean particle diameter and a BET value are the same as that of the apatite carbonate powder A and B and abbreviation, they are not elaborated in a temperature requirement (600 ** - 900 **). The carbonic-acid-group content same like the apatite-carbonate powder E as the apatite-carbonate powder A and B: If mean particle diameter and a BET value become the outside of the range specified by this invention even if it has 10.90 % of the weight, in a

temperature requirement (600 ** - 900 **), it will not sinter at all.

[0022] If it is in the sintered compact obtained again using the apatite carbonate powder A according to this invention, it has the sintered compact characteristic which excelled [within the limits / whose calcination temperature is 600 ** - 850 **] in all.

[0023]

[Effect of the Invention] This invention is made to sinter at low temperature comparatively using the apatite carbonate powder excellent in low-temperature-sintering nature so that clearly from the above explanation, From the place which is what obtains the target apatite carbonate sintered compact, such an apatite carbonate sintered compact, It becomes the sintered compact material which contains a carbonic acid group comparable as the living body hard tissue, and has a structure similar to the living body hard tissue and which was extremely excellent in biocompatibility, and is very useful as a bone or the filler for teeth, supplementation material, etc.

[Translation done.]